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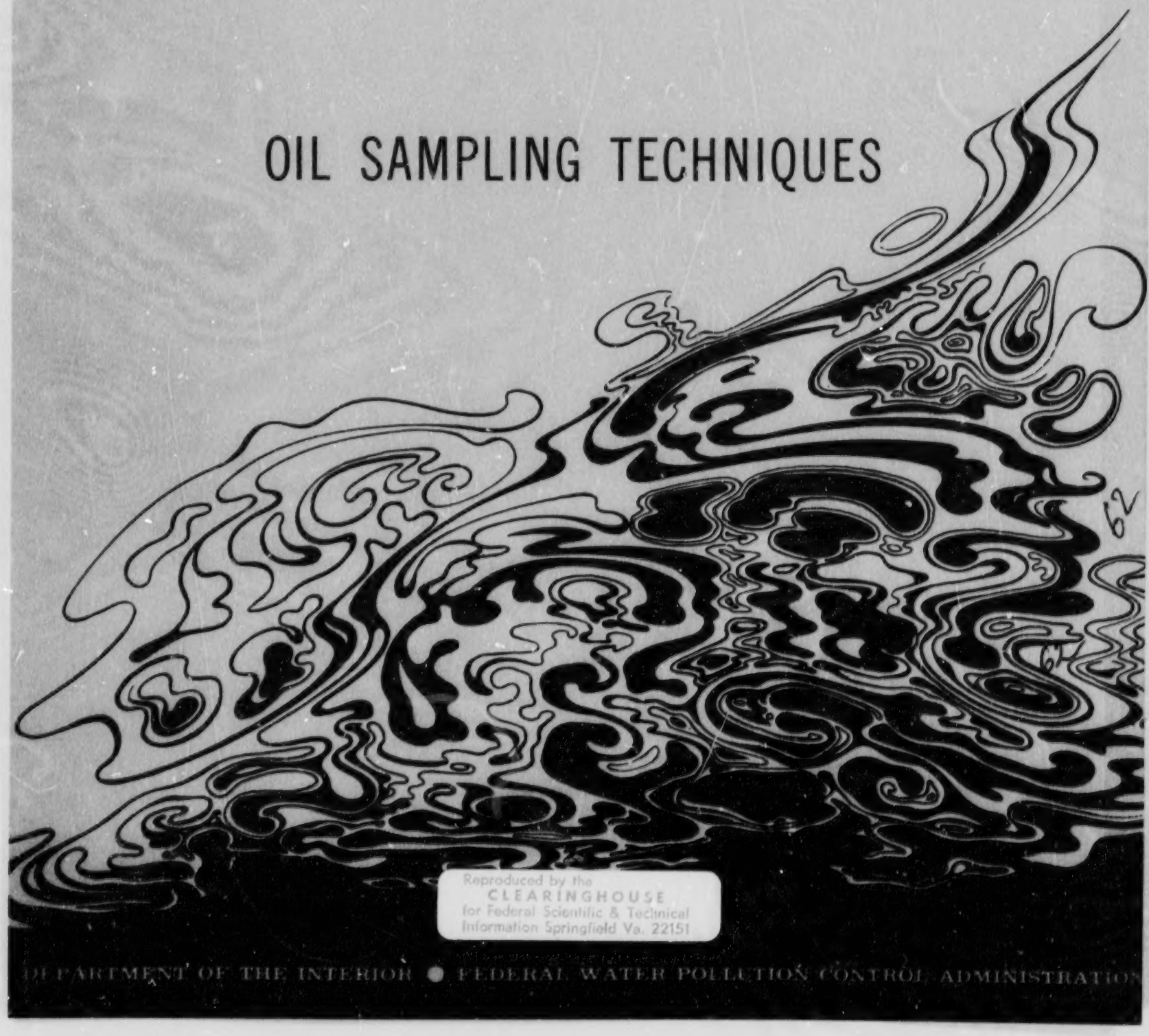
OIL SAMPLING TECHNIQUES



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WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Reports describe the results and progress in the control and abatement of pollution of our Nation's waters. They provide a central source of information on the research, development and demonstration activities of the Federal Water Pollution Control Administration, Department of the Interior, through inhouse research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

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PROGRESS REPORT:

OIL SAMPLING TECHNIQUES

Compiled By

Oil & Hazardous Materials Research Section
Northeast Region Research and Development Program
Edison Water Quality Laboratory
Edison, N. J. 08817

for the

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
U. S. DEPARTMENT OF THE INTERIOR

Oil Pollution —— 15080QBJ 12/69

December 1969

FWPCA Review Notice

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ABSTRACT

Sampling of oil in the environment, depending upon the thickness of the slick, can present certain operational problems, most paramount of which is the collection of an adequate volume of sample required for identification by chemical analyses. Several basic "dip-stick" techniques, which are primarily applicable for sampling slicks with a thickness of greater than 2 mm, as well as suggested methods for sampling thin oil slicks are discussed and illustrated. Included in this report are preliminary results on oil entrapment by solid absorbents obtained by the Oil & Hazardous Materials Research Section, Edison, New Jersey. Also reported are results of investigations performed by foreign and U. S. scientists, using various types of sampling equipment and materials.

KEY WORDS: Oil, Sampling, Absorptior, Separation

INTRODUCTION

This report provides a description of selected methods known to be available for obtaining representative samples of "thin" (less than 2 mm thick) oil slicks in the water environment. The purpose of presenting these techniques is not to recommend any one method of sampling; but rather, to make available the latest technical information to personnel concerned with the problem of collecting representative samples of oil slicks. Needless to say, the methods outlined in this report supplement the already known basic "dip-stick" methods for sampling heavy or thick oil slicks. Some of these techniques, which were discussed in the publication "Laboratory Guide for the Identification of Petroleum Products", January, 1969, are repeated in this report for purposes of continuity.

Regardless of what method is used for sampling, it is important that a chain of custody of the samples be properly maintained and recorded from the time the samples are taken until the litigation is completed. In this regard, a record of time, place, and name and title of the person taking the sample, and each person handling the sample thereafter must be maintained and forwarded with the sample, using Form No. FWPCA 208 (7-68).

Many precautions must also be observed when handling oil samples for analyses since the character of the sample may be affected by a number of common conditions including:

a) composition of the container —— glass bottles should always be used since plastic containers, with the exception of teflon, have been found under certain conditions to absorb organic materials from the sample. In some cases, the reverse is also true in that compounds have been dissolved from the plastic containers into the sample itself. This problem also applies to the bottle cap liners; therefore, the portion of the cap that comes in contact with the sample should be made of glass, teflon, or lined with aluminum foil;

b) cleanliness of the container —— previously unused glass bottles are preferred. If this is impossible, bottles should be either acid cleaned or washed with a strong detergent and thoroughly rinsed and dried;

c) time lapse between sampling and analysis —— since the chemical characteristics of most oils, especially the lighter fuel oils, change with time, the time lapse between sampling and analysis should be kept to a minimum. If analysis cannot be completed within 24 hours, samples can be preserved, depending upon the volatility of the oil, by removal of air and exclusion

of light. With heavier type oils, such as No. 4 and residual oils, carbon dioxide may be used to displace the air. If dry ice is available, (approximately 0.5 cu. in.) it may be added to the sample. As soon as the effervescing has stopped, the jar should be sealed. When carbon dioxide or another inert gas is not available, or in those instances where volatile components are present (No. 2 or lighter), the sample can be preserved by carefully filling the bottle to the top with water to displace the air. All samples should be kept under refrigeration until analyses are completed;

d) collection of adequate volume of sample —— it is desirable to obtain as much of a sample of the oil as possible. It is suggested that 20 mls be considered as the minimum volume of oil needed to perform a series of "identification analyses" on light oils —— No. 2 and below. For heavier oils a minimum volume of 50 mls is required.

As additional data on sampling oil in the environment are forthcoming, material will be released in the form of addendums to this progress report. After reading this report, any individual who has knowledge of, or who has developed a sampling technique, is urged to make this information available to the Oil & Hazardous Materials Research Section, Edison, New Jersey 08817.

Preliminary Study on the Use of Solid Absorbents

S E C T I O N - I

Oil and Hazardous Material Research Section
FWPCA, Edison, New Jersey, 1968

PRELIMINARY STUDY ON THE USE OF SOLID ABSORBENTS

EDISON, NEW JERSEY, 1968

I. Background

Before oil portions obtainable from an oil slick are chemically analyzed in the laboratory, the first and most important requirement is to secure a representative sample of the slick. It is therefore apparent that the chemical nature of the oil should not be altered irretrievably by the sampling techniques and furthermore there should be no contamination of the sample introduced by components of the sampling device.

Sampling of oil presents many difficulties not immediately obvious. An oil slick may vary in thickness from several inches down to a monomolecular layer measured in microns (10^{-4} cm.). The quantity of sample required is therefore important since such will determine the area of sweep. For example, 5,000 gallons of oil, if assumed to be evenly distributed over one square mile of water, will equate to an oil thickness of 0.0071 mm. If 200 ml of sample is found necessary, then all the oil must be recovered from 28 square meters of open water. If sampling recovery is 50 percent rather than 100 percent, the sweep area must be doubled. Table I below describes theoretical thickness and area, assuming an even distribution of oil for various magnitude oil spills.

TABLE I

Oil Distribution on a Water Surface

Spill Area Gal/Sq.Mile	Spill Area ml/Sq. Meter	Area (Sq. Meters) Req'd. to obtain 200 ml/sample	Oil Thickness (mm)
1,000,000	1430	0.14	1.43
100,000	143	1.4	0.143
10,000	14.30	14	0.0143
5,000	7.15	28	0.0071
1,000	1.43	140	0.00143 = 1.43μ
100	0.143	1400	0.000143 = 0.143μ

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Prior to initiating studies at Edison, New Jersey, it was determined that the ideal sampler should have the following characteristics:

a) simplicity
b) ability to function under various conditions
c) few moving parts
d) low cost
e) rapid recovery
f) no secondary treatment required in recovering the sample

Because of these specifications, mechanical devices using pumps and motors were eliminated from consideration. Likewise, the use of chemicals was precluded due to possible change of oil characteristics. This led to emphasis and application of solid absorbent materials for recovery of oils from the water environment.

II. Experimental

A. Screening of Absorbent Materials

The following materials were evaluated to determine their effectiveness in removing oil from water.

a) Teflon shavings
b) Polypropylene fiber
c) Rayon manufacture waste material
d) Glass-fiber insulation ("Rockwool")
e) Styrofoam
f) Polyurethane foam

Whereas first-stage studies showed each of the above materials capable of recovering oil from water, the polyurethane foam showed greatest promise for absorbing larger volumes of oil. Also, the polyurethane foam in sheet form could be easily handled and did not disperse over the water surface as did certain of the other absorbent materials. Thus, further investigations were undertaken using only this particular "sorbent".

B. Testing of Polyurethane Foam

Polyurethane foam was employed in sheet form in varying thickness of 1/8-inch, 1/4-inch, and 1-inch.

C. Polyurethane Foam Characteristics

a) Foam A*

Size	:	1 ft.^{2} x 1/4"
Volume	:	36 inch^3
Volume	:	590 cm^3
Dry Weight	:	15.9 g
Density	:	0.027 g/cm^3
Saturated water volume	:	540 ml
Residual Oil retained after squeezing	:	17 ml

b) Foam B*

Size	:	85 inch^2 x 7/8"
Volume	:	74 inch^3
Volume	:	1210 cm^3
Dry weight	:	22.8 g
Density	:	0.011 g/cm^3
Saturated water volume	:	900 ml
Residual oil retained after squeezing	:	11 ml

c) Foam C*

Size	:	44.6 inch^2 x 1"
Volume	:	44.6 inch^3
Volume	:	732 cm^3
Dry weight	:	15.5 g
Density	:	0.0212 g/cm^3
Saturated water volume	:	620 ml
Residual oil retained after squeezing	:	7 ml

D. Experimental Results

Table II shows the pertinent data obtained upon use and recovery of South Louisiana Crude. During these preliminary studies no attempt was made to control temperature, wind, degree of mixing slick area, water makeup (tap water used) or other variables that might affect the inherent characteristics of the crude oil on a water surface.

*Names and sources of Polyurethane Foams are retained in the files of the Oil & Hazardous Materials Research Section, Edison, New Jersey.

TABLE II

Results of Oil Recovery Experiment Using Polyurethane Foams

Oil Available (mls)			Recovery of Oil (mls)			Recovery of Oil (%)		
A	B	C	A	B	C	A	B	C
50	40	30	40	30	20	80	75	67
100	140	145	60	100	105	60	71	72
240	210	280	145	115	185	60	55	66
475	555	665	225	305	415	48	55	62
580	1090	895	130	645	450	22	59	50
1345	1565	1495	380	600	530	28	38	35
1365			410			30		

Oil absorbency plots are defined in Figures 1, 2 and 3 respectively for Foams A, B and C. Although data are not included in this report, the foams demonstrated significantly higher recovery after one use. The oil-laden foams after the initial "run" could absorb a much greater amount of oil compared to the previously unused or "fresh" foam.

To detect possible changes in the character and composition of oil via pickup, infrared spectra analysis was conducted on the oil before and after pickup. No differences were apparent by IR, although further verification of this reaction would be desired by means of chromatographic separation techniques. The oily mixture recovered from the foams after passing through the wringer and gravity separation showed less than 0.1 percent water.

E. Conclusions

Based upon limited experimentation it was found that polyurethane foam is an effective material for absorbing oil from the surface of water. Future work should be directed towards determining optimum conditions for oil removal. Additional study should include, but not necessarily be limited to:

a) determining effect of foam thickness on oil pickup
b) determining effect of pore size (density of foam)
c) determine feasibility of pre-treatment with oleophilic substances
d) testing with different grades of oil
e) further field applications

On the basis of this preliminary study, it is suggested that polyurethane foam sheets could be used to sample "thin" oil slicks. In actual practice, several square feet of polyurethane foam can be attached with staples to a wooden dowel or other rigid, floatable device. The foam-holding device in turn is attached to a line fixed to a pole. The sampler (in fisherman style) would steer or drag the sheet of polyurethane through the oil slick and after a few minutes of contact time would remove the foam from the water. The foam is passed through a wringer, the oil collected and the process repeated until a sufficient quantity of sample is obtained.

(Figures 4-6) are photographs taken of a unit field-tested and found to be successful. The system although simplified greatly, offers considerable promise and plans are underway to improve this sampling approach.

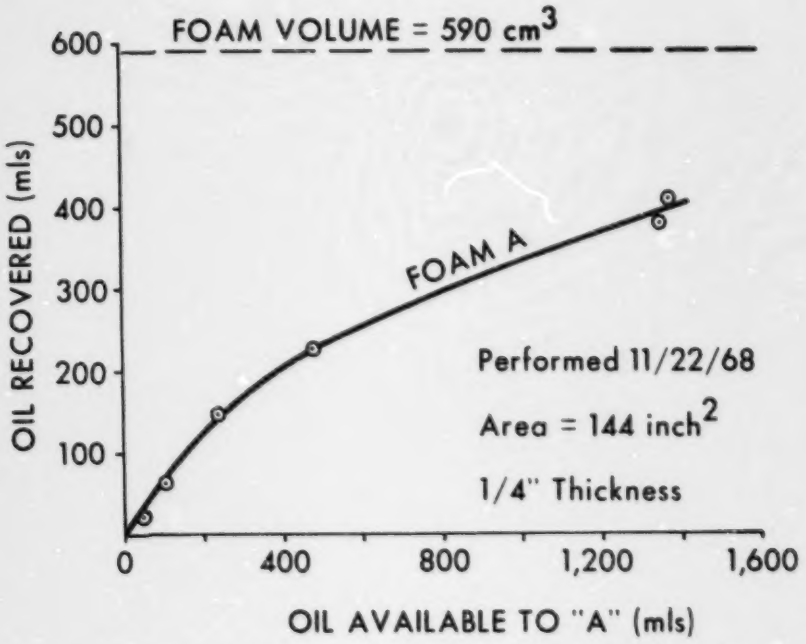

FIGURE 1-Absorbence of South Louisiana Crude Oil by Polyurethane Foam A

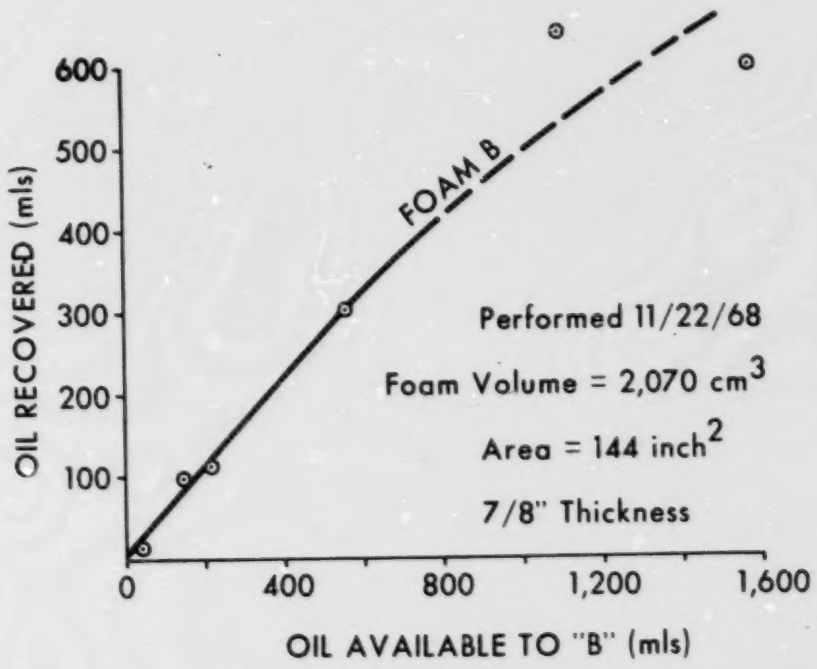

FIGURE 2-Absorbence of South Louisiana Crude Oil by Polyurethane Foam B

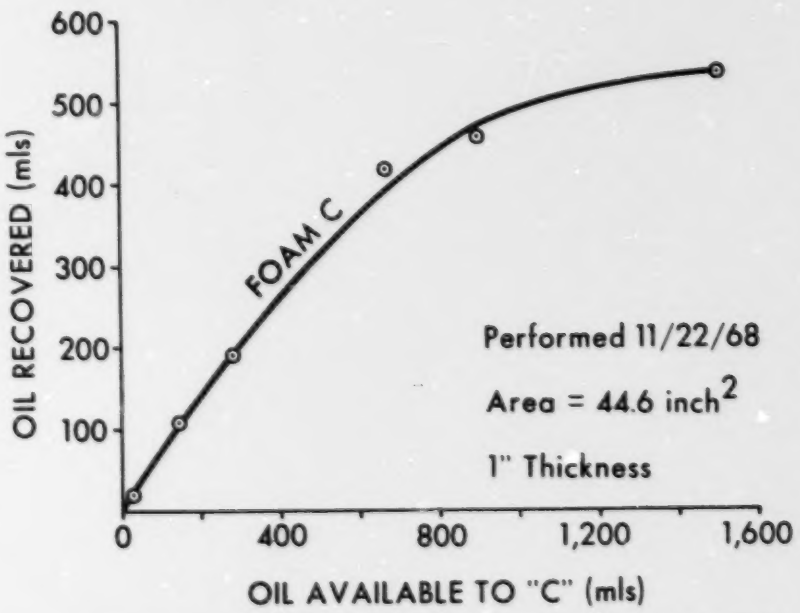

FIGURE 3-Absorbence of South Louisiana Crude Oil by Polyurethane Foam C

Figure 4: Strips of polyurethane, which can vary in thickness from 1/8 to 1-inch, are permanently fastened at one end to a wooden dowel which in turn is connected via a cord to a "fishing pole".

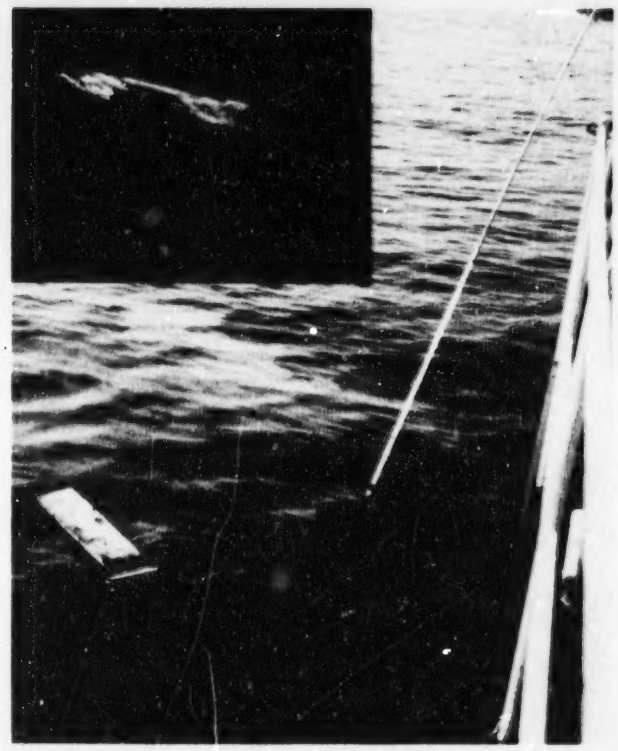

Figure 5: Foam sampler floats on water surface. Back and forth motion of "fishing pole" moves sampler through oil slick causing absorption of oil into void areas of polyurethane foam.

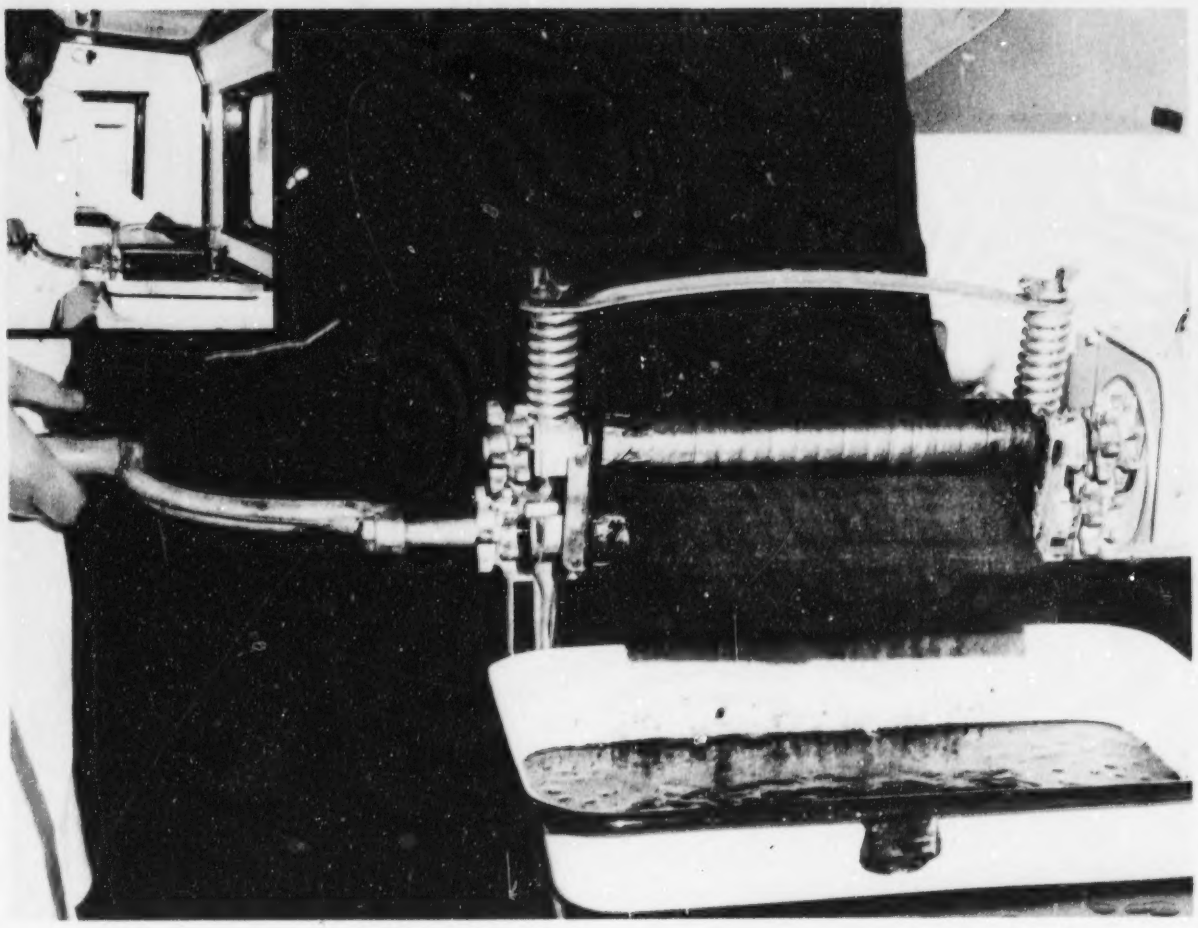

Figure 6: Garage-type wringer is used to "squeeze-out" oil entrapped within polyurethane sampler. Oil-water mixture collected in tray is transferred to separatory funnel and then to glass sample bottle.

Oil Sampling Methods

By

Fred K. Kawahara, Ph.D., F.A.I.C.

U. S. Department of the Interior
Federal Water Pollution Control Administration

S E C T I O N - II

Oil Sampling Methods

By

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The sampling techniques outlined below were included in the publication "Laboratory Guide for the Identification of Petroleum Products", January, 1969.

"Oily materials may be collected from the surface of the water by means of three devices. The first is a glass, wide-mouth filtering funnel, connected by teflon tubing to a two-way stopcock. Volatile oil product found upon the water surface is ladled with the aid of this device; the lower water phase is discarded by opening the stopcock. The upper petroleum phase is transferred to a large container. Ladling and water-discard operation should be repeated until a sufficient amount of oil (10 grams or more) is collected.

An alternative collector is a paint-free dustpan with a suitable stopcock attached to the handle. Collection and concentration of several grams of petroleum product can be achieved with this household device. Heavy, viscous material, such as asphalts, can be collected in a similar manner. Transfer to the final collecting jar from the funnel, jar, or dustpan, is possible with aid of a clean spoon or stick.

The third device is a large household mop with a wringer attachment. It is suggested that, before use, the sponge, whether derived from natural or synthetic materials, be rinsed thoroughly with a proper solvent, such as chloroform. This mop is passed through the oil pool; the absorbed materials are squeezed out and transferred by means of a funnel into the collecting jar. The sampling operation is facilitated by attaching the bottle, scoop, or mop to a long pole. Where possible, reference samples of oil should also be obtained from vessels or shore facilities."

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Oil Slick Collecting Device

By

Admiralty Materials Laboratory
British Royal Navy, 1969

S E C T I O N - III

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Oil Slick Collecting Device
Admiralty Materials Laboratory
British Royal Navy, 1969

Information has been obtained from sources in the United Kingdom concerning a highly-promising oil slick sampling device developed by the Admiralty Materials Laboratory of the Royal Navy. Following the Torrey Canyon incident, the Laboratory was assigned responsibility for investigating the distribution of oil over large water areas. Part of this work involved the sampling of thin oil slicks. It has already been reported that collection of such oil layers is far from simple because in many cases visible slicks are exceedingly thin and, furthermore, it is difficult to separate sufficient material for eventual analysis.

The Laboratory has reportedly designed a device for collecting samples of oil from thin slicks which currently is under Patent application. The device depends upon the principle whereby when water is stirred in a cylindrical vessel the surface assumes the shape of a parabola, and oil together with other free-floating matter, will collect near the center of rotation. The oil collector consists of an open-ended cylinder with a stirrer inside. After the device is lowered into the water, the oil collecting at the center of the cylinder is trapped in a central tube and retained when the cylinder is withdrawn from the water. It may be possible to extend this application of recovering small oil portions to the larger task of scavenging oil slicks spread over broad areas in harbors, estuaries, and possibly open waters. Further information is being requested on this sampling technique.

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Sampling in Waters Polluted by Hydrocarbons. Part I

by

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Cebedeau Laboratory

S E C T I O N - IV

English Translation Made From
Tribune Cebedeau (Centre Belge Etude Doc. Eaux)
16, No. 234, 257-261 (1963)

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Sampling in Waters Polluted by Hydrocarbons. Part I

I. Introduction

The quantitative determination of hydrocarbons in waters is a difficult problem because the aim is to determine a whole range of products at the same time.

Most of the time, current methods make use of hydrocarbon solubility in ether or carbon tetrachloride, which makes it necessary to determine hydrocarbons and lipids simultaneously as well as all the other compounds that may be present in the water and are soluble in ether.

The problem of collecting samples is even harder to solve, especially if we consider the variety of forms that hydrocarbons can assume in water. First of all, there are hydrocarbons present as a distinct phase, in the form of a surface film. These surface films are obtained by spreading one liquid on another with a higher surface tension. This spreading can proceed all the way to a monomolecular film. In the case of hydrocarbons (surface tension of the order of 30-35 dynes/cm), the forces of cohesion oppose unlimited spreading, and we have so-called "coherent" films.

This film often contains suspended lipophilic matter, which stabilizes the film depriving it of some of its mobility. Hydrocarbon films present certain problems: danger of ignition, failure to show, obstruction of apparatus, interference with gas exchange between water and atmosphere, etc. It is therefore of interest to determine this category of hydrocarbons separately. We also find hydrocarbons and greases within the body of the water, not in the dissolved state, to be sure, but in the form of emulsions, sometimes very fine and very stable, or incorporated in small aggregates of suspended matter. In this form, they are especially troublesome for waste water purification plants and for plants treating a water supply, either human or industrial.

It is obvious that hydrocarbon distribution in water is anything but homogeneous, especially if the aggregates in which they are incorporated are relatively large. It should be noted that the two main forms in which hydrocarbons are found are interconvertible to a certain extent. The observation of waste waters from rolling mills, which are highly polluted by oils, has shown that aggregates loaded with drops of oil can be maintained in suspension by agitation, but as soon as a decrease in turbulence occurs, such aggregates will come to the surface, wherein the oil immediately spreads in an iridescent film.

We will not speak of the difficulties involved in recovering the last traces of greases or hydrocarbons on the bottles used for sampling; we will assume this problem has been satisfactorily solved. We shall content ourselves in this first paper with comparing various sampling methods reported by specialized laboratories*.

---

*A second paper deals with specific methods proposed by Cebedeau.

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When we questioned the principal western laboratories studying waters, we received as many different responses as there were laboratories consulted. Many of these answers gave evidence that the problem of sampling hydrocarbons had not been recognized as such. Many others could be considered variants of the same basic operating procedure. For each method described below, ten tests were made, either in the laboratory or under "on-the-spot" operating conditions. These series of quantitative determinations allow us at best to evaluate the reproducibility of the measurements for each of the methods, none of which seem worthy at this time of being considered a reference method. Until a fuller inquiry, we consider the best method to be that which consistently gives the highest results. For the methods applicable to surface films and involving only a small sampling surface, sampling was done from films made artificially in the laboratory —— which will give an idea of the absolute value of the sampling carried out by these methods.

II. Selected Methods

A. Determination of the Surface Film

1. Camphor Test

(Origin: Deutsche Einheitsverfahren H 17/18)

This test consists in observing particles of camphor placed on the surface of the water. If these particles are in a state of incessant agitation, there is no greasy film on the water. If, on the other hand, they remain motionless, there is a film. This test is a qualitative test. This phenomenon, known as the "camphor dance", corresponds to the formation of a surface film from the solid product.

2. Pail With Tap

(Origin: RIZA, Rijksinstituut voor Zuivering van Afvalwater)

The sampling is done in a pail equipped with a tap at the bottom; wait five minutes after sampling, then draw off and collect the last liter with the greases and hydrocarbons of the surface film. Rinse the pail with petroleum ether. Refer the measurement to the cross section of the pail. If necessary, repeat several times to collect sufficient material.

B. Collection of a Representative Sample

1. Simple Pail

(Origin: EAWAG - Eidg. Anstalt für Wasserversorgung, Abwasserreinigung und Gewässerschutz)

Collect about 5 liters from the surface layer using an ordinary pail.

2. Sliding Cylinder

(Origin: Shell and American Petroleum Institute. Method 702-53)

This ingenious apparatus permits rapid collection of a 2-liter representative sample of water, including the surface film, to a depth of about 50 cm. The apparatus has (See Figure 1) a sliding Plexiglas cylinder whose fall is controlled by a trigger. In falling vertically, the cylinder cuts a cylinder in the water similar to a core sample. At the bottom of its travel, it meets a stopper, which hermetically seals it and permits withdrawing it from the water. In principle, the apparatus is not suitable for depths greater than 0.5 m. We found a less interesting version of this method in The Analyst 81, 492 (1956), recommended by the Joint ABCM-SAC Committee on Methods for the Analysis of Trade Effluents.

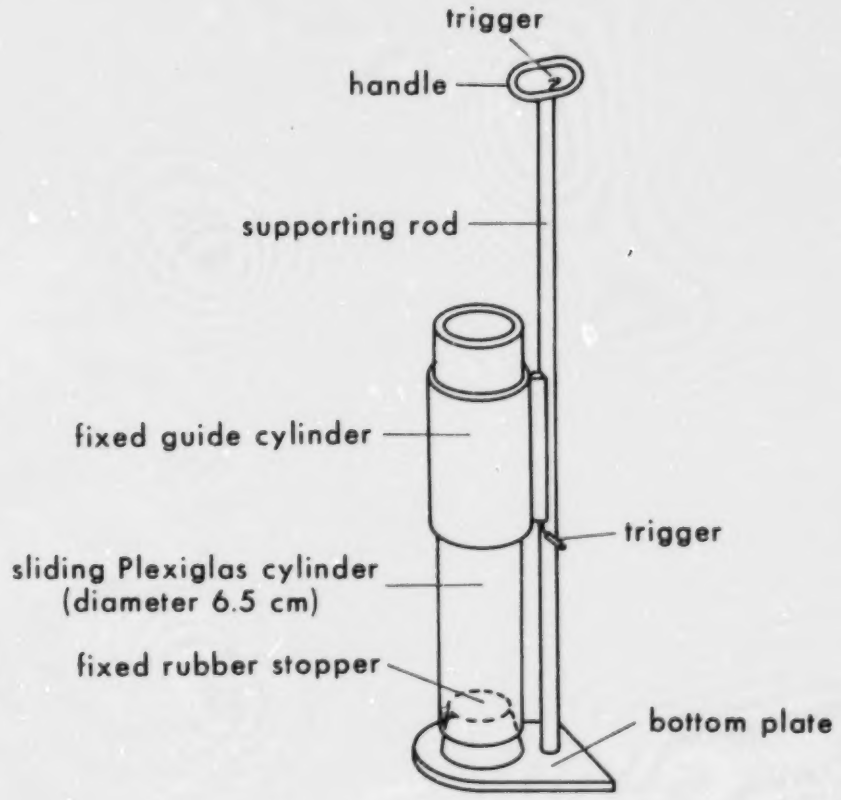

FIGURE 1-Sliding cylinder.

3. Movable Probe With Pumping

(Origin: EAWAG - Bundesanstalt für Gewässerkunde)

The apparatus used consists of a long plastic tube 1/2 inch in diameter, weighted at the end and provided with colored reference marks every 25 cm. The tube runs in a peristaltic pump operated by a 6-v storage battery. The probe is lowered to the bottom of the water to be sampled, and the probe is raised by a steady movement. The corrections needed to take into account the volume of water contained in the tube are made.

C. Measurement Results

1. Note on the Statistical Presentation of Results

Our tables show the n measurements of x made in each series. For these measurements, the various statistical parameters are calculated below:

Mean: the arithmetic mean of all the measurements ($\bar{x}$).

Standard deviation: the square root of the variance where

$$\sigma = \sqrt{\frac{\Sigma\{x - \bar{x}\}^2}{n - 1}}$$

There are about 2 chances out of 3 that a result picked at random will have a deviation $\leq \sigma$ with respect to the mean.

Standard deviation in %: the standard deviation expressed in % of the mean $\bar{x}$.

Mean deviation: calculated by the formula:

$$\sigma_m = \frac{\sigma}{\sqrt{n}}$$

There are about 2 chances out of 3 that the exact value sought, for which n measurements are made, will fall in the interval $x \pm \sigma_m$. We give σ_m for 10 measurements.

95% deviation: equal to 1.96 σ. There are 95 chances out of 100 that an isolated measurement will not differ from the value sought by a deviation greater than this number.

2. Determination of the Surface Film

a. Camphor Test

The tests were made in the laboratory on hydrocarbon films of known dimensions. For this, we placed on a container of known surface area increasing amounts, measured by microburette, of used SAE 20 crankcase oil, filtered beforehand. The films are characterized by the number of milligrams of hydrocarbon present per square meter of surface. The same process was repeated for all the laboratory tests. The test is said to be:

positive (+) when the camphor grains remain perfectly motionless;

doubtful (±) when they exhibit alternating motion and lack of motion;

negative (-) when they remain incessantly in motion.

Table I below compiles the results obtained and shows that this test, for the hydrocarbon employed, actually permits determining that a film belongs to one or another of the three categories delimited by the following values:

from 0 to 175 mg/m^2
from 175 to 325 mg/m^2
above 325 mg/m^2

TABLE I

mg/m^2	Result
454	+
341	+
336	+
331	+
327	+
322	+ -
318	+ -
295	+ -
272	+ -
250	+ -
227	+ -
204	+ -
182	-
159	-
136	-
114	-
23	-

However, when we repeated this test with a more fluid hydrocarbon such as petroleum residuum, we observed a new phenomenon, which falsified the results. The camphor grains are denser than the hydrocarbons, but less dense than water, and they normally position themselves at the interface between the two liquids. At this point, however, they tend to form a surface film, too. The camphor has no difficulty in driving back a film of petroleum residuum, even a thick one. This is why we observe the camphor dance on light and fluid hydrocarbon films. In the case of a heavier oil, this phenomenon does not occur, and the method can be used.

b. Addendum Relative to the Camphor Test

We believe it is of interest to complete this analysis of the camphor test with Table II drawn from the literature, where appearance of various iridescent hydrocarbon films is described. Since the amounts of hydrocarbons were given in liters per km^2, we converted them to mg/m^2, assuming a density of 0.92.

TABLE II

Visual Description of Oil Slick Correlated With Thickness
(Taken from Gas and Wasserfach 82, 182, 1939)

Hydrocarbons			
ml/m^2	mg/m^2	Thickness mm	Appearance
36.5	33.5	0.0365	Scarcely visible under the best conditions
73	67	0.073	Visible - silver luster
146	134	0.146	First traces of color
292	268	0.292	Visible bright-colored bands
975	897	0.975	Duller colors
1950	1790	1.950	Dark colors
>40	> 37	> 0.040	Continuous iridescent film

c. Pail With Tap

Tables III and IV present the two series of results obtained at two points in the water lines of a plant (rolling mill). The results are very poor, even in Series IV where we benefit from a surface of calm water.

TABLE III

Reproducibility Results Using Pail With Tap Method, Point A

Measurement No.	mg/m^2	
1	205	
2	428	
3	578	Mean: 601 mg/m^2
4	1120	Standard deviation: ± 520 mg/m^2
5	816	Standard deviation, %: ± 86.5%
6	133	Mean deviation of 10 measurements: ± 164 mg/m^2
7	181	95% deviation: ± 1019 mg/m^2
8	398	
9	1590	
10	260	

TABLE IV

Reproducibility Results Using Pail With Tap Method, Point B

Measurement No.	mg/m^2	
1	1040	
2	137	
3	193	Mean: 1400 mg/m^2
4	177	Standard deviation: ± 8380 mg/m^2
5	8870	Standard deviation, %: ± 598%
6	1210	Mean deviation of 10 measurements: ± 2650 mg/m^2
7	319	95% deviation: ± 16,425 mg/m^2
8	758	
9	870	
10	437	

3. Collection of a Representative Sample

a. Simple Pail

The results obtained with this method, which has the advantage of extreme simplicity, are not very constant, as may be judged from Table V.

TABLE V

Reproducibility Results Using Simple Pail Method

Measurement No.	mg/m^2	
1	15.7	
2	15.0	
3	11.9	Mean: 12.35 mg/liter
4	6.4	Standard deviation: $\pm$ 6.30 mg/liter
5	3.5	Standard deviation, %: $\pm$ 51.0%
6	15.6	Mean deviation of 10 measurements: $\pm$ 2.0 mg/liter
7	26.0	95% deviation: $\pm$ 12.35 mg/liter
8	8.0	
9	12.0	
10	9.4	

b. Sliding Cylinder (Shell)

This method is the most convenient and reproducible. It does not seem possible to modify it to permit sampling at depths greater than 50 cm. Still, it is very likely that series of tests would show that the water layer between 0 and 50 cm depth is the most important from the viewpoint of the hydrocarbon content. These tests have not been made. Table VI gives the measurement results.

TABLE VI

Reproducibility Results Using Sliding Cylinder Method

Measurement No.	mg/m^2	
1	5.44	
2	3.64	
3	3.57	Mean: 4.22 mg/liter
4	4.68	Standard deviation: $\pm$ 0.734 mg/liter
5	3.91	Standard deviation, %: 17.4%
6	3.64	Mean deviation of 10 measurements: $\pm$ 0.232 mg/liter
7	5.07	95% deviation: $\pm$ 1.44 mg/liter
8	4.85	
9	3.31	
10	4.13	

c. Movable Probe With Pumping

Contrary to what we thought, this method proved highly unsatisfactory. We think one of the reasons for this lies in the use of a very long tube for sampling (10 m), which calls for pumping for some time before collecting the sample, if we wish to be certain that the sample comes from the desired depth. But in the case of abundant suspended matter, it may well not be moved along the tube at the same velocity as the liquid. Furthermore, the weighted tube touches the bottom of the water before being drawn up; consequently, it produces an eddy that may resuspend the deposits. Finally, the suction of the pump itself contributes to the formation of turbulence. Perhaps it is possible to remedy these drawbacks, at least in part. We have not tried to do so, for this method also has the disadvantage of calling for a heavy piece of equipment that is hard to handle. Table VII shows the results of our measurements.

TABLE VII

Reproducibility Results Using Movable Probe Method

Measurement No.	mg/m^2	
1	2.30	
2	0.90	
3	5.30	Mean: 4.06 mg/liter
4	6.10	Standard deviation: $\pm$ 2.65 mg/liter
5	2.10	Standard deviation, %: $\pm$ 65.3%
6	7.60	Mean deviation of 10 measurements: $\pm$ 0.84 mg/liter
7	1.90	95% deviation: 5.19 mg/liter
8	1.00	
9	6.80	
10	6.60	

III. Conclusions

The first conclusion we can draw from this comparative study (a conclusion that an analytical chemist cannot fail to draw) is that all the methods in the collection are deplorably poor. The best would not satisfy even the least exacting person. It is, however, a fact with which we shall have to reckon and for which we should be forewarned by multiplying the number of samples taken.

For the purpose of tentatively classifying the different methods tested, we have drawn up Table VIII which contains the standard deviations in per cent and also gives the number of samples that must be taken in order to be certain (threshold of 0.95) that the mean of the measurements on the sample will not deviate more than 25% (or 50%) from the actual value. This table contains only the most favorable series for the methods, which have been the object of several series of measurements.

TABLE VIII

Statistical Comparison of Various Methods

	Standard deviation, %	No. of measurements necessary (see text)	
		50%	25%
Determination of the surface film			
Pail with tap.	86.5	12	47
Collection of a representative sample			
Sliding cylinder	17.4	1	2
Simple Pail	51.0	4	16
Movable probe with pumping . .	65.3	7	26

According to the table, it does not seem at all possible to retain the method of the "pail with tap" for the determination of the surface film. This is why Cebedeau is particularly eager to find another method. This research will be the subject of a forthcoming paper*. The semiquantitative camphor test is to be retained only for heavy hydrocarbon films.

*This paper is given immediately following in this compilation of reports on sampling.

Sampling in Waters Polluted by Hydrocarbons. Part II

by

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Cebedeau Laboratory

S E C T I O N - V

English Translation Made From
Tribune Cebedeau (Centre Belge Etude Doc. Eaux)
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Sampling in Waters Polluted by Hydrocarbons. Part II

I. Introduction

Several months ago, when making a study of stream pollution by hydrocarbons, Cebedeau had occasion to work on the problem of collecting samples, certainly a practical problem, and of relevance to the interests of this meeting. (Topic No. 23, "Practical Measures to be Taken for the Prevention of Pollution by Mineral Oils in Ports".)

Questions asked of the principal western laboratories brought us as many different answers as there were laboratories consulted. We have already reported the results of a special study of these methods (1). Because these methods do not satisfy us we have designed still other methods in the Cebedeau Laboratories to be described here with a brief critique of their application.

II. Methods Designed at Cebedeau

A. Determination of the Surface Film

1. Filter Paper Disks

Sampling is accomplished by throwing flat on the water a loose-textured filter paper disk of the usual dimensions available on the market (diameter 9 or 11 cm). Such a filter can be wetted either by water or by hydrocarbons, but once wetted by one, it no longer retains the other liquid. It is therefore important to place this paper flat on the water (this confines the use of the method to calm waters) and to remove it with caution with the aid of tweezers, also limiting the running of water over the filter, which would cause an error by loss of materials.

2. Movable Frame

For sampling, we use a square wooden frame exactly 1 m on a side. The fourth side of this frame is movable (See Figure 1) so that after a 1 m^2 film has been intercepted on the surface of the water, we can bring this surface to 1 m x 0.2 m, and finally collect the film in a wide-necked bottle opening just below the surface.

3. Metal Cylinder Lined with Filter Paper and Repulsion by a Surface-Active Solution

Use is made of a copper cylinder 7 cm tall, with a circumference slightly smaller than the side of a sheet of chromatographic paper (i.e., a diameter of about 17.5 cm) (See Figure 2). This cylinder is provided with a handle and a 5 mm side hole. It is lined with a strip of chromatographic paper (loose-textured paper) which is carefully applied to the metal and attached by small clamps.

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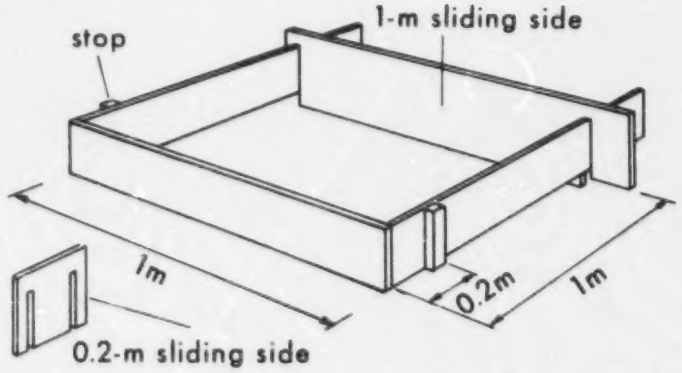

FIGURE 1-Moveable frame

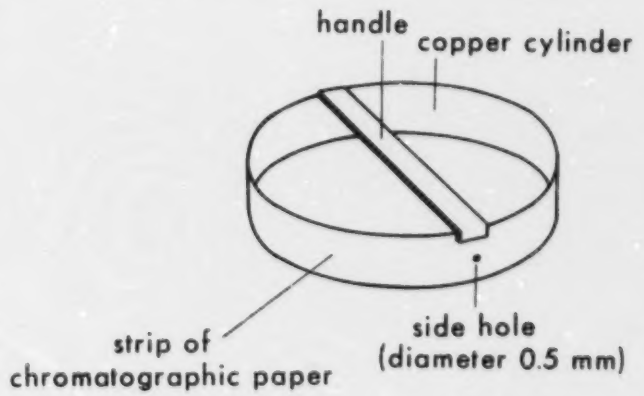

FIGURE 2-Filter aspiration device

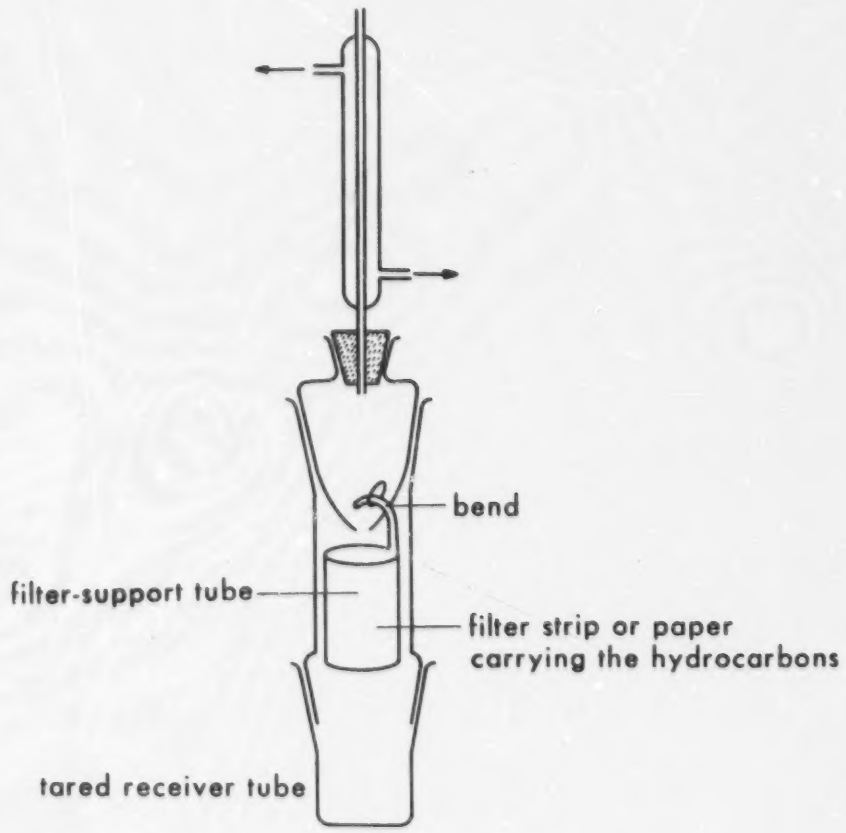

FIGURE 3-Semimicroextractor

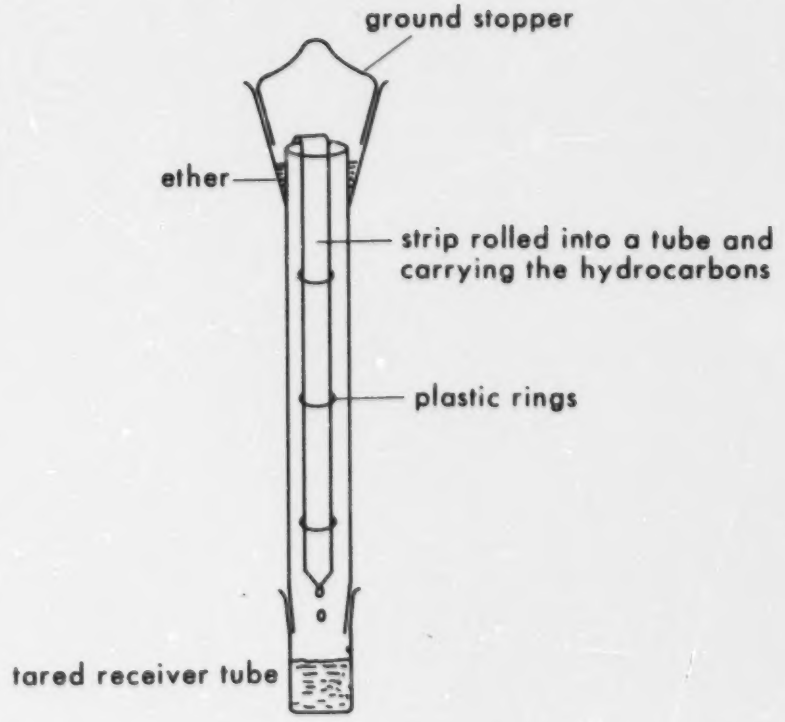

FIGURE 4-Chromatographic tube

Before sampling, the strip is completely impregnated with distilled water. Excess water is applied and runs over the paper. From this point on, the clamps become useless and may be removed.

In sampling, the apparatus is plunged into the water and immersed to within a centimeter of the upper edge of the strip of paper. At this time, one or two drops of a concentrated solution of commercial detergent are rapidly applied by means of a dropper to the surface of the water at the center of the intercepted circle. This produces a surface-active film that tends to drive the hydrocarbon film toward the periphery of the apparatus (which is easily discernible).

When the hydrocarbon film is confined to the peripheral ring 1 or 2 cm wide, the apparatus is taken out of the water by a steady and very slow movement, which has the effect of "aspirating" the hydrocarbon film onto the strip of filter paper. The apparatus is then set vertically, with the side opening on the bottom, and so as to avoid any running of water outside the strip. The water is absorbed by a wad of cotton placed outside the hole. The strip may then be detached, dried, and hydrocarbons removed from the paper. To recover the hydrocarbons, we can extract them hot with petroleum ether in a semi-microextractor (See Fig. 3) of the Quickfit type, or elute them cold in a chromatographic tube (See Fig. 4).

III. Measurement Results

A. Note on the Statistical Presentation

Our tables present n measurements of x made in each series. For these measurements, we calculated the various statistical parameters below:

Mean: the arithmetic mean of all the measurements ($\bar{x}$);

Standard deviation: the square root of the variance where

$$\sigma = \sqrt{\frac{\Sigma\{x - \bar{x}\}^2}{n - 1}}$$

There are about 2 chances out of 3 that one result taken at random will have a deviation $\leq |\sigma|$ with respect to the mean.

Standard deviation in %: the standard deviation expressed in % of the mean $\bar{x}$.

Mean deviation: calculated by the formula:

$$\sigma_m = \frac{\sigma}{\sqrt{n}}$$

There are about 2 chances out of 3 that the exact value that we want to determine and for which we make n measurements will fall in the interval $x \pm \sigma_m$. We give σ_m for 10 measurements.

95% deviation: equal to 1.96 σ. There are 95 chances out of 100 that an isolated measurement will not differ from the value sought by a deviation greater than this number.

B. Determination of the Surface Film

1. Filter Paper Disks

For these tests we used Schleicher and Schüll SS 5893 filters 12.5 cm. in diameter with a surface area of 123 cm^2 for the tests in the laboratory, and filters 11 cm. in diameter with a surface area of 95 cm^2 for the industrial plant tests. The results of the laboratory tests are given in Table I. The tests performed in the plant were made on a settling basin for rolling-mill waste water, at a point chosen for its mild surface agitation. These results are given in Table II.

TABLE I

Reproducibility Results Using Filter Paper Disk Method, Laboratory Tests

No.	Measurement, mg/m^2	
1	642	
2	527	
3	263	Mean: 562 mg/m^2
4	663	Standard deviation: $\pm$ 138 mg/m^2
5	505	Standard deviation, %: $\pm$ 24.6%
6	537	Mean deviation for 10 measurements: $\pm$ 43.7 mg/m^2
7	453	95% deviation: $\pm$ 270 mg/liter
8	758	
9	684	
10	589	

TABLE II

Recovery of Oils From Industrial Plant Using Filter Paper Disk Method

No.	mg/m^2 Introduced	mg/m^2 Recovered	Deviation, %	
1	2190	2570	+ 17.4	
2	1815	1700	- 6.4	
3	1580	1650	+ 4.4	Mean: 90.8%
4	1329	1484	+ 11.7	Standard deviation: ± 19.15%
5	1117	841	- 24.7	Standard deviation,%: ± 21.1%
6	994	837	- 15.8	Mean deviation for 10 measurements: ± 6.06%
7	872	748	- 14.2	95% deviation: ± 37.53%
8	763	643	- 15.7	
9	671	403	- 39.9	

In Table II we have made a statistical analysis of the percentages. We see that in the range of films tested (from 650 to 2200 mg/m^2 we recover on the average less hydrocarbon than introduced: 90.8% vs 100%. This suggests a systematic error of the order of -10%, but statistical theory does not allow us to call this deviation significant. The precision or reproducibility is somewhat better in the laboratory, which is entirely normal.

The difficulty of this method is obviously in the removal of the filter after impregnation. In spite of the use of tweezers and the speed, a certain amount of water running over the filter cannot be avoided, causing material loss.

2. Movable Frame

Test results using the Movable Frame Method shown in Table III were quite unsatisfactory, due especially to the difficulty of recovering the hydrocarbons adhering to the walls of the frame.

TABLE III
Reproducibility Results Using Movable Frame Method

No.	Measurements, mg/m^2	
1	259	
2	487	
3	26.3	Mean: 172 mg/m^2
4	22.3	Standard deviation: ± 238 mg/m^2
5	50.3	Standard deviation, %: ± 138%
6	390	Mean deviation for 10 measurements: ± 75.2 mg/m^2
7	616	95% deviation: 466 mg/m^2
8	20.4	
9	28.4	

3. Metal Cylinder Lined with Filter Paper and Repulsion by a Surface-Active Solution

Two series of measurements were made at different points.* The first series given in Table IV was carried out by a more experienced operator than the second series given in Table V. It is to be hoped that the scatter of the results will be reduced by repeated practice with the method.

*Further description of the nature of samples and type of oils was not provided in the translation of the report.

TABLE IV

Reproducibility Results Using Filter Aspiration Device, Point A

No.	Measurements, mg/m^2	
1	236	
2	134	Mean: 249 mg/m^2
3	220	Standard deviation: ± 69.4 mg/m^2
4	285	Standard deviation, %: ± 27.9%
5	315	Mean deviation for 10 measurements: ± 22.0 mg/m^2
6	338	95% deviation: ± 136 mg/m^2
7	216	

TABLE V

Reproducibility Results Using Filter Aspiration Device, Point B

No.	Measurements, mg/m^2	
1	314	
2	212	
3	342	Mean: 422 mg/m^2
4	358	Standard deviation: ± 205 mg/m^2
5	322	Standard deviation, %: ± 41.8%
6	298	Mean deviation for 10 measurements: ± 64.9 mg/m^2
7	318	95% deviation: ± 402 mg/m^2
8	607	
9	897	
10	554	

The hydrocarbons can be recovered by cold elution or by hot extraction. Cold elution gives unstable results, for its duration varies greatly from sample to sample. Table VI shows unsatisfactory results obtained from two different series of measurements. Here we are dealing with an intermediate stage in the treatment of the sample, and we can only assume that it introduces single or double errors.

TABLE VI
Cold Elution Recovery

No.	Measurements, mg A	B
Theoretical	53.8	-
1	44.8	13.6
2	49.3	11.2
3	50.7	8.1
4	50.2	13.8
5	55.0	10.2
6	51.6	6.3
7	44.9	7.6
8	-	8.5
9	-	8.2

In recovery by hot extraction, we determined the minimum duration that would assure complete extraction of a sample and concluded that a two-hour extraction was sufficient.

Sample deposited on the strip	38.5 mg
Recovered after 1/2 hour	27
Recovered after 1 hour	31.6 mg
Recovered after 1-1/2 hours	35.25 mg
Recovered after 2 hours	35.25 mg

It remained to check the sampling methods in the hot extraction technique on films of known density. The results of 5 measurements are presented below (Table VII). Compared to the other methods, these results are highly satisfactory. We believe that the variability of the result should be attributed not to the sampling itself (which is virtually quantitative) but to the difficulty of preparing exactly similar films.

TABLE VII
Hot Extraction Recovery

No.	Measurements, mg	
1	25.90	Theoretical amount to be recovered: 26.15 mg
2	21.05	Average amount recovered: 24.35 mg
3	26.00	Standard deviation: ± 2.06 mg
4	23.70	Standard deviation, %: ± 8.46%
5	25.10	Mean deviation for 10 measurements: ± 0.65 mg
		95% deviation: ± 4.04 mg

IV. Conclusions

For the purpose of classifying the different methods tested, we compiled Table VIII, which lists the standard deviations in per cent and also gives the number of samples that must be taken in order to be certain (threshold of 0.95) that the mean of the measurements on the sample does not deviate more than 25% (or 50%) from the actual value. This table contains only the most favorable series for the methods, which were the object of several series of measurements. It was concluded that the first two methods could be retained.

TABLE VIII

Sampling Methods — Summary

Determination of the Surface Film	Standard Deviation, %	No. of Measurements Needed 25%	50%
Metal cylinder lined with filter paper	8.46	1	1
Filter paper disks.	24.6	1	4
Wooden frame.	138	30	118

Literature Cited

(1) Edeline, F., and Heuze, R., "Sampling in Waters Polluted by Hydrocarbons", Tribune Cebedeau (Centre Belge Etude Doc. Eaux) 16, No. 234, 257-261 (1963).

Collection of Slick-Forming Materials from the Sea Surface

by

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S E C T I O N - VI

The following materials are taken from two separate reports prepared by Dr. W. D. Garrett on the same subject. The first paper was in the form of a manuscript submitted February 14, 1962 as Project SF 001-06-01, Task 1500 in response to NRL Problem O03-17. The second paper appeared in Report of NRL Progress, March 1965 issue.

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Collection of Slick-Forming Materials from the Sea Surface

I. Introduction

Aggregations of surface-active materials on large natural bodies of water such as rivers, bays, and the oceans are often responsible for visible alterations in the appearance of the surface. These surface-active substances can originate from man-made sources, but they may also arise from products of the marine biosphere. Whatever the source, these polar-nonpolar substances accumulate at the surface and are compressed by the convergent action of wind and water into areas in which wind-induced capillary waves are damped. The calmed area or "sea slick" stands out in contrast to the background water body since skylight reflectance from the slick is altered by its action in damping the capillary waves.

The physical properties of slicks and their responses to environmental changes have been studied by several investigators. Adam (1) developed a spreading drop method for the measurement of ocean surface film pressures in situ. Lumby and Folkard (2) applied such spreading oil measurements to slicks in order to study the effect of air movement and currents on the film pressure of the slick. Some of the physical properties of sea slicks have been studied by Ewing (3) while Dietz and LaFond (4) noted the predominance of calmed areas of the sea in the vicinity of water possessing high biological activity.

The objective of this research was to develop a technique to collect and recover the constituents of natural oceanic slicks so that the chemical composition of the responsible film-forming materials could be established and be used to develop a physical and chemical picture of the ocean surface.

II. Preliminary Survey of Techniques

Laboratory research was conducted toward the development of an effective field method for the collection of the surface-active chemicals responsible for sea slicks. Film-pressure measurements have indicated that areas of the ocean in which capillary waves are damped often consist of only slightly compressed monomolecular layers of surface-active substances. Film pressures as low as 2 to 4 dynes/cm. were found in clearly visible slicks, and values rarely exceeded 10 dynes/cm. To obtain a sufficient quantity of the surface film material for identification and study in the laboratory, it was necessary to collect the film from a large area of the water surface. In addition, it was desirable for the method chosen to be as independent as possible of film pressure so that large areas of film could be removed efficiently even when the surface pressure was low.

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A chemical characterization of the oily material extracted by Timmons and Jarvis (5) from plankton taken from the near-surface water of the Bay of Maine showed that they consisted of considerable proportions of C_{16}, C_{18}, C_{20}, and C_{22} fatty acids and their triglycerides. Since plankton organisms are ubiquitous in the world's oceans, it was assumed that chemicals of this type would in part constitute many natural slicks.

For these reasons, methods for the removal of monolayers of oleic acid, stearic acid, and plankton oil from the surface of both distilled and synthetic sea water were examined. The plankton oil used in this work was extracted from a near-surface plankton collection made in May of 1960 in the North Atlantic Ocean (40°N, 71°W). The plankton were primarily Calanus. The oil extracted from them has been kept under refrigeration and the method of extraction was the same as that used by Timmons and Jarvis (5).

The monolayers were spread at various degrees of film compression on water contained in a Pyrex glass hydrophil tray filled with a Cenco float-type torsion head. A monolayer was spread and a waxed glass barrier was moved toward the floating torsion head barrier compressing the film to the desired film pressure. Film retrieval was attempted and a barrier was again advanced in the direction of the torsion head to restore the original pressure. The resulting decrease in area of the monolayer at constant pressure was a measure of the quantity of material which had been removed.

Preliminary studies with mineral oil as a floating absorbent for the slick-forming materials proved unsuccessful because no significant amount of organic monolayer was found to dissolve into the oil. Furthermore, an approach of this nature was not considered promising since any water-insoluble material which would dissolve a surface-active chemical from a water surface would have its own spreading pressure increased. It would no longer exist as a lens but would spread out over the water and make recovery difficult.

A series of solid materials in sheet form were contacted horizontally with various monolayers. The solid sheets were held firmly in a metal frame which was immersed parallel to the water surface on which the monolayer was spread. The candidate adsorbers included clean glass, aluminum foil, nylon, polyethylene, Plexiglas, polyvinylfluoride, glass paper (one micron fiber diameter), Teflon, and bondable Teflon (one side treated with sodium in liquid ammonia). The Teflon and polyvinylfluoride polymers exhibited no capacity for adsorption of the monolayers. The glass, nylon, Plexiglas, aluminum foil, and glass paper removed an area of monolayer equal to the area of the solid in contact with the liquid surface.

Two adsorbers, polyethylene and activated polytetrafluorothylene (treated with sodium in liquid ammonia) appeared most promising. However, this technique was also discarded because of the inability to desorb the collected organic material by solvent washing. Other disadvantages inherent in this method were limited adsorptive capacity, possibility of desorption onto areas of water containing no surface film, and selective adsorption.

III. Screen Collection Method

Experiments with 16 mesh (16 wires per inch) window screen indicated that segments of the surface of a liquid were removed intact when a screen was placed either in horizontal contact with or drawn vertically through the liquid surface. In this manner many small discrete areas of the surface film between the wires could be trapped and lifted from the bulk water. Any materials contained in the entrapped surface film were also carried along. When the screen was drawn through the liquid with its plane parallel to the surface, complete independence from film pressure variations was achieved. Although some adsorption occurred on the screen wires, the main mechanism for film removal was the entrapment between the wires.

Film-balance experiments showed that a monolayer could be transferred from a water surface by draining the screen entrapped liquid into a collection vessel. The results of the effect of mesh size on this procedure are summarized in Table I. As the number of wires per unit area increased, the operation of the screen approached that of a solid adsorber. In these measurements, metal screens of various mesh sizes were contacted with a synthetic sea water surface covered with an oleic acid monolayer at a film pressure of 5 dynes/centimeter. The screen was removed and drained into an open vessel and the operation was repeated. After each contact the film balance barrier was advanced to restore the original 5 dynes/centimeter surface pressure. The area swept by the barrier was then equal to that removed by the screen. In the case of the 16-mesh screen, the apparent screen efficiency dropped to a value of approximately 75 percent after the first surface contact and remained constant thereafter. In the case of the tighter screens, the efficiency decreased to a lower value because a larger wire area was available for adsorption while less open space existed for water entrapment. It is also seen that the first contact with the surface removed a greater area of monolayer since both adsorption and water-entrapment mechanisms were operating. After the first contact, little further adsorption occurred. When the distance between the wires became large, as in the case of the 4-mesh screen, the trapped-water film became unstable and ruptured almost immediately before transfer could be effected.

TABLE I

Removal of Monolayers from Water Surfaces by Metal Screens*

Monolayer-Oleic acid on synthetic sea water

Film pressure- 5 dynes/cm

Screen (Mesh)	Surface Contact Number	Area of Monolayer Removed (cm^2)	Area of Screen (cm^2)	Screen** Efficiency (%)	Open Space of Screen (%)
4	Water film between screen wires ruptures almost immediately				
16	1	99.6	100	99.6	60.2
	2	74.4		74.4	
	3	73.1		73.1	
	5	74.4		74.4	
	10	75.0		75.0	
30	1	114.0	120	95.0	40.8
	2	57.8		48.2	
	3	49.2		41.0	
	5	46.5		38.7	
80	1	74.0	85	87.1	19.4
	2	32.2		37.9	
	3	21.4		25.2	
	5	19.9		23.4	

*Screens drained into separate container after each surface contact.

**Area of monolayer removed divided by area of screen.

By using this technique with a 16-mesh screen, oleic acid, stearic acid, and plankton oil monolayers were retrieved from a sea water surface at pressures ranging from 1 to 10 dynes/cm. Since the screen efficiency was approximately 75 percent for all of the film pressures studied, there was no apparent dependence of the method on the degree of compaction of the monolayers within these ranges. It was determined experimentally that a 0.15 mm-thick layer of water was collected by the 16-mesh screen made from 0.14-mm diameter wire.

IV. Field Collection Equipment

A 16-mesh Monel screen of 0.014 inch diameter wire containing 60.2 percent open space was incorporated into a 30 by 24 inch aluminum frame. Two 30-inch aluminum handles of 3/4 inch rod were bolted onto the frame. In practice the screen was placed through the water surface. It is then withdrawn horizontally (parallel to water) through the water surface and drained immediately into a sample bottle as illustrated in Figure 1. This procedure is repeated until the sample bottle is filled. Approximately 200 to 250 surface contacts are required to collect a 5-gallon sample, which corresponds to a sea surface area of from 1000 to 1250 square feet per sample.

V. Verification of Screen Collection Method

The screen collection procedure was verified in a 17-foot tank by the following experiment. A compressed oleic acid monolayer was spread onto the surface water on one side of a paraffin wax-coated cord. The experimental situation depicted in Figure 2 shows the positions of the floating cord before the commencement of monolayer retrieval. When the surface of the tank was almost completely covered by monolayer, as indicated by the position of the cord (area I), a drop of oleic acid was placed on the remaining uncovered surface (area II). This lens acted as a monomolecular piston to drive the barrier cord back across the tank as the oleic acid monolayer in area I was removed by the screen entrapment method. As the monolayer was retrieved the barrier moved across the tank decreasing the area of I. From the number of screen contacts and an estimation of the area of monolayer removed, it was determined that the screen method was about 70 percent area efficient in continued use. This figure is in good agreement with the film-balance data recorded in Table I for the 16-mesh screen.

The fact that 100 percent efficiency is not attained is due to an initial adsorption of a portion of the monolayer onto the screen wire. This material remains adsorbed onto the screen wires, thereby deactivating the metal so that additional adsorption does not occur during the remainder of the sampling operation. A number of these experiments were performed until a 5-gallon container was filled with the water-oleic acid mixture. By calculation, 55 milligrams of oleic acid had been removed. Concentration and recovery of the oil yielded 38 milligrams of material.

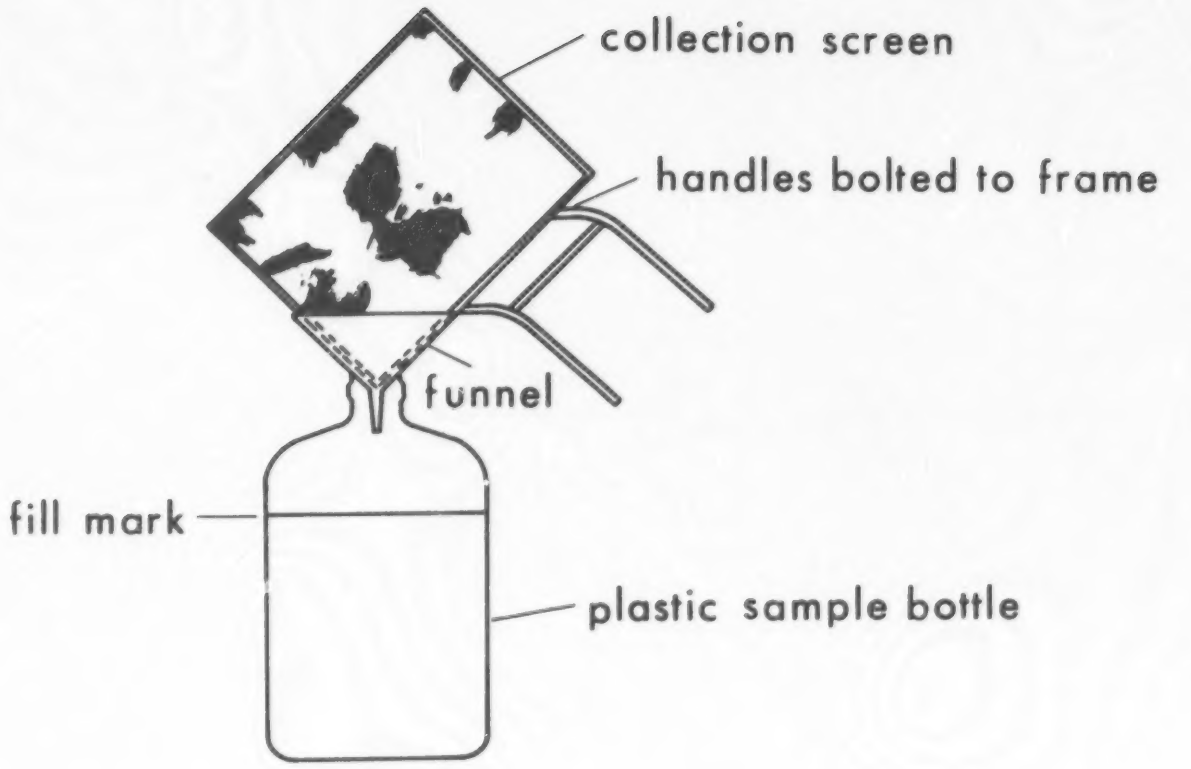

FIGURE 1-Sea-surface collection assembly in draining position

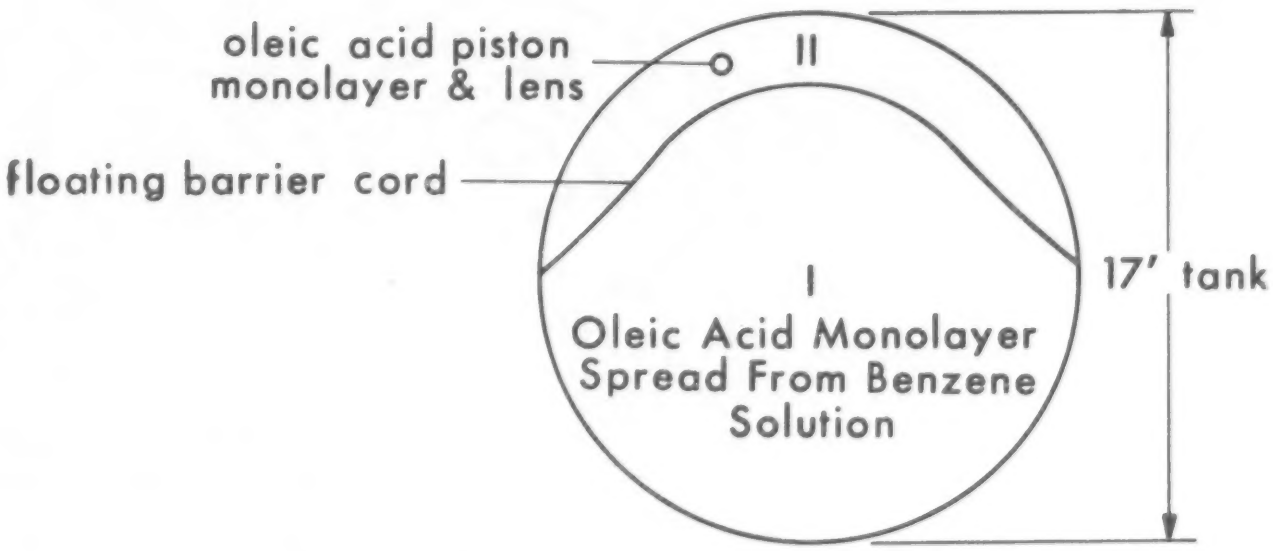

FIGURE 2-Top view of tank experiment to study monolayer retrieval method

Field verification was obtained by retrieving a condensed monolayer of oleic acid which had been spread on the Chesapeake Bay. No natural slick was apparent in the area to give a background film as interference. Processing the 4-gallon sample collected yielded 19 milligrams of oleic acid. The yield was somewhat reduced by large quantities of silt present in the samplewhich when filtered off removed oleic acid by adsorption.

The method was also applied to a natural slick of unknown origin on Chesapeake Bay. Film-pressure measurements using Adam's spreading drop method varied from 3 to 12 dynes/centimeter and averaged 5 dynes/centimeter in the slick. The water beneath the surface was unusually clear for this body of water and little silt appeared in the sample. Approximately 27 milligrams of surface-active material was isolated from the 5-gallon sample. The multi-component mixture was separated by selective solubility in various solvents. The chemical and physical properties of the collected slick and its constituents will be included in a future report on the constitution of natural slicks sampled at various stations in the Atlantic and Pacific Oceans, the Bay of Panama, and the Gulf of Mexico.

These experiments demonstrated that it was possible to collect significant quantities of materials which are spread out upon the sea surface in monomolecular thicknesses, making possible the retrieval of sea slick material in concentrated form.

VI. Summary

A method for the removal and isolation of the substances present in natural and man-made oceanic oil slicks had been developed. The technique utilizes a planar metal wire screen which when drawn through a water surface removes discrete segments of the surface layer between the wires. In this manner, a 0.15-mm film of surface water containing all constituents of the surface film may be collected. This approach is found to be effective regardless of the film pressure; hence, it may be applied to monolayers under low film compression.

Addendum on Isolation and Analysis of Collected Organic Material

In sampling, the screen enclosed in a metal frame with handles is placed into the water parallel to the surface, withdrawn, and drained into a collection vessel. The resulting concentrate of polar material and sea water is further concentrated by the subsequent precipitation of a ferric hydroxide sol within the sample bottle. The organic constituents are occluded and adsorbed by the resulting gelatinous precipitate which after settling is separated from the sea water. The concentrate is acidified to dissolve the ferric hydroxide and extracted with various solvents. The solvents are pumped off under vacuum leaving behind the nonvolatile surface-active materials of which the slick was composed.

A procedure has been developed for the concentration and separation of the collected slick constituents from the background sea water. The technique was preliminarily studied by Jeffrey and Hood (6) who found that 95% of a complex mixture of all organic material derived from an algae culture was coprecipitated with a ferric hydroxide gel. This approach has also been recently reported by Williams (7) as a method for the concentration of organic acids in sea water samples. The following is the procedure used in this Laboratory for the isolation of slick material.

The pH of the sample is adjusted to about 8.0 with sodium carbonate solution. Then 50 mg of ferric chloride per liter of sample is added with stirring from a 1% solution. To obviate cumbersome filtration, the resulting sol is allowed to settle for several hours and the supernatant water is siphoned off. The sol is then acidified with 1:1 hydrochloric acid to a pH of 2.0, with stirring until the ferric hydroxide dissolves. A deep yellow but generally clear solution results. The mixture is then extracted with several 100-ml portions of organic solvent. The solvent is pumped off under vacuum at ambient temperatures to avoid thermal modification of the solute. The solvents used should be freshly distilled and contain no appreciable residue upon evaporation. Solvents used in this work were petroleum ether, benzene, ether, and chloroform.

Experimentally, the above procedure was found to be about 70% efficient when benzene or petroleum ether was used in the solvent extraction step. Hundred-mg portions of oleic acid, dodecyl alcohol, and plankton oil were dissolved separately in 5 ml of acetone and dispersed into separate 5-gallon containers of synthetic sea water. Recovered from the mixture by the foregoing procedure were 75 mg of oleic acid, 65 mg of dodecyl alcohol, and 68 mg of plankton oil.

Centrifugation was used as an alternate method for the isolation of the slick material. It was found that most of the organic materials are adsorbed onto any particulate matter present in the sea water sample. These solids and biological entities are thrown out onto the wall of the centrifuge cylinder from which the organic matter may be removed by solvent extraction. The centrifugate is then treated by the ferric chloride precipitation method to retrieve any substances not removed by centrifugation.

Ideally it is desirable to collect only those chemicals contributing to the slick phenomena. To remove the undesired biological entities, silt, and flotsam from the collected surface chemicals, the Chesapeake Bay samples were passed through a motor-driven Sharples super centrifuge. A continuous-feed cylinder was driven at 23,000 rpm developing 13,200 g at the cylinder wall. When the clear centrifugate was extracted with organic solvents less than 1 mg of organic material was isolated. A duplicate sample was collected from the same bay slick. This sample was not centrifuged and yielded 12.8 mg of organic materials by extraction. Solvent treatment of the solids collected on the centrifuge cylinder from the centrifuged sample resulted in a 13.7 mg collection of chemicals whose infrared spectra approximately matched the spectra obtained for the materials from the uncentrifuged sample.

The centrifuge removed not only the particulate matter but also most of the surface-active matter by adsorption onto the discontinuous phase. Thus, the centrifuge appeared to be a tool for the isolation of the slick constituents from the background sample water. A liner of clean aluminum foil was inserted into the centrifuge bowl to facilitate the removal of the collected solids. After centrifugation of the sample, the liner is removed and washed with solvent to dissolve and desorb the adherent surface-active materials.

In the event that the collected sample does not contain sufficient particulate matter to adsorb the surface-active constituents, it is recommended that all centrifugates be treated with ferric chloride as detailed in the preceding section.

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27 Abstract

Sampling of oil in the environment, depending upon the thickness of the slick, can present certain operational problems, most paramount of which is the collection of an adequate volume of sample required for identification by chemical analyses. Several basic "dip-stick" techniques, which are primarily applicable for sampling slicks with a thickness of greater than 2 mm, as well as suggested methods for sampling thin oil slicks are discussed and illustrated. Included in this report are preliminary results on oil entrapment by solid absorbents obtained by the Oil & Hazardous Materials Research Section, Edison, New Jersey. Also reported are results of investigations performed by foreign and U. S. scientists, using various types of sampling equipment and materials.

Abstractor

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